

SOLUTOCAPILLARY CONVECTION EFFECTS ON POLYMERIC MEMBRANE MORPHOLOGY

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FY96 Task Accomplishments

The following progress has been made in addressing the tasks listed above:

1. Specification of membrane-casting solutions: The composition range of the casting solutions (cellulose acetate, acetone, water) has been determined to satisfy the criteria of low-gravity experimentation: macrovoid formation occurs, and phase inversion occurs in less than 20 seconds. Steps have been added to the preparation of the solutions, namely controlling water content using molecular sieves and controlling polymer molecular weight using ultracentrifugation, in order to make the polymer solutions stable and predictable.
2. Design and construction of the test cells: Four flight-qualified test cells were constructed. Each membrane-casting apparatus ("MCA") is capable of automatically casting 6 membranes 1 cm in diameter having depths ranging from 80 to 259 μm . Mass transfer of evaporating acetone is extremely rapid, being driven down a steep gradient by adsorption in a 100-fold excess of activated carbon. The exact transfer rate is being determined from a modified comprehensive model (described in the attached final report). The reaction is initiated by pulling a trigger and allowing a sliding block to spread the casting solution during a period of several milliseconds. Phase inversion occurs in less than 20 seconds, and the membranes are subsequently dried. This process is tracked by optical monitoring using a bifurcated fibre optic and measuring reflected light from the surface of the casting cell. The fibre-optic data are accumulated simultaneously with g-sensor and parabola-count data on a personal computer. This real-time measurement capability for studying membrane formation in low g is novel and represents an added feature which we did not anticipate in our original proposal. It has added significantly to the value of the data.
3. Perform ground-based control experiments: Numerous membranes have been cast in the laboratory using the MCAs, and the conditions for forming macrovoids, as evaluated by scanning electron microscopy (SEM), are reproducible.
4. Carry out low-g experiments in KC-135 flights: Mr. Konagurthu completed all of the pre-flight physiological and medical procedures and is qualified to perform experiments on NASA's KC-135 low-g aircraft. Subsequent to guidance from Dr. Owen and from the BioServe Space Technologies Center staff, he assembled supporting flight hardware and performed low-g experiments for three days. About 50 membranes were cast during low g, 2-g and level flight. The results were clear: membranes cast in low g were saturated with macrovoids, some of which completely perforated the membrane; membranes cast in 2 g were, according to our observations, lacking in macrovoids; membranes cast in level flight were the same as on the ground -- a moderate incidence of macrovoids. These results are consistent with our original suggestion that solutocapillary flow, and not diffusion, is the cause of macrovoid formation.

5. Carry out structural characterization of membranes: SEM has been used to quantitate the incidence of macrovoids and to seek any other unusual characteristics. The only usual characteristic observed so far is "tunneling macrovoids", those that completely penetrate the membrane resulting in a straight hole from one side to the other.

6. Model development and corroboration: A coupled heat- and mass-transfer model has been developed in conjunction with the experimental research. It consists of a combined Fortran code by Shojaie and SPRINT subroutines by Berzins. It has been adapted to account for heat and mass transfer in low g, and also the physical casting conditions. The model predictions were corroborated using the reflectometry data obtained and also via a laser interferometry technique developed specifically for the MCA casting mechanism. The interferometry experiments were conducted in order to obtain instantaneous film thickness changes as a function of time, and the model predictions agreed quite well with the experimental data.

FY96 Bibliographic Citations by NASA MSAD Task PI's

Proceedings:

Konagurthu, S., Krantz, W. B. and Todd, P. "Use of low g to test alternative hypotheses for macrovoid growth in polymeric membranes. Proc. of Euromembrane '95, Vol. 1, 256-261 (1995).

Presentation:

Konagurthu, S., Krantz, W. B. and Todd, P. "Experimental studies of hypotheses for macrovoid formation in polymeric membranes" presented at the Annual Meeting of the Southwest and Rocky Mountain AAAS Regional meeting, July 1994.
(The student won the first place award for the best student presentation)

Presentation:

Konagurthu, S., Krantz, W. B. and Todd, P. "Use of low g to test alternative hypotheses for macrovoid growth in polymeric membranes. " presented at the Euromembrane '95 Conference, Bath, England, September 1995.

Presentation:

Konagurthu, S., Todd, P. and Krantz, W. B. "Mechanism of macrovoid formation during polymeric membrane casting". Lifes Sciences and Space Medicine Conference '95, American Institute of Aeronautics and Astronautics, Houston TX, April 1995.

Presentation:

Konagurthu, S., W.B Krantz, A.R. Greenberg, and P. Todd, " A Novel Approach to Test Alternative Hypotheses for Macrovoid Growth in Polymeric Membranes," Eighth Annual Meeting of the North American Membrane Society, Ottawa, Canada, May 1996.

(The student won the first place award for the best student paper awarded by the NAMS technical committee)

ABSTRACT

Macrovoids are undesirable large pores in membranes used for purification. They form when membranes are cast as thin films on a smooth surface by evaporating solvent (acetone) from a polymer solution. There are two untested hypotheses explaining the growth of macrovoids. One states that diffusion of the non-solvent (water) is solely responsible, while the other states that solutocapillary convection is the primary cause of macrovoid growth. Solutocapillary convection is flow caused by a concentration induced surface-tension gradient. Macrovoid growth in the former hypothesis is gravity independent, while in the latter it is opposed by gravity. To distinguish between these two hypotheses, experiments were designed to cast membranes in zero-gravity. A semi-automated apparatus was designed and built for casting membranes during the 20 secs of zero-g time available in parabolic aircraft flight such as NASA's KC-135. The phase changes were monitored optically, and membrane morphology was evaluated by scanning electron microscopy (SEM). These studies appear to be the first quantitative studies of membrane casting in micro-gravity which incorporate real-time data acquisition. Morphological studies of membranes cast at 0, 1, and 1.8 g revealed the presence of numerous, sparse and no macrovoids respectively. These results are consistent with the predictions of the solutocapillary hypothesis of macrovoid growth.

1 Introduction

1.1 *Polymer membrane casting*

The ever-changing world demands new materials, alternative energy resources, more efficient processes, and environmentally safer industries. With increased environmental awareness and the rising cost of fossil energy, scientists are forced to explore various widening avenues in order to meet these new challenges. Synthetic polymeric membranes represent a relatively new technology which is capable of providing more efficient and environmentally safer separation processes. Polymeric membranes have become attractive alternatives to many energy-intensive separation processes. The pioneering work of Loeb and Sourirajan (1962) permitted development of highly selective polymeric membranes while maintaining commercially viable fluxes. The majority of polymeric membranes can be formed via a process referred to by Kesting (1985) as a "phase transition/inversion" process by which a polymer solution (in which the solvent is the continuous phase) inverts into a swollen three-dimensional macromolecular network or gel (where the polymer is the continuous phase). A pictorial representation of this phase inversion process as suggested by Kesting is shown schematically in Figure 1. Phase transition

can be induced by solvent evaporation (the dry-cast process), nonsolvent/solvent exchange (the wet-cast process), cooling (the thermal-cast process), and polymer leaching (the polymer-assisted process).

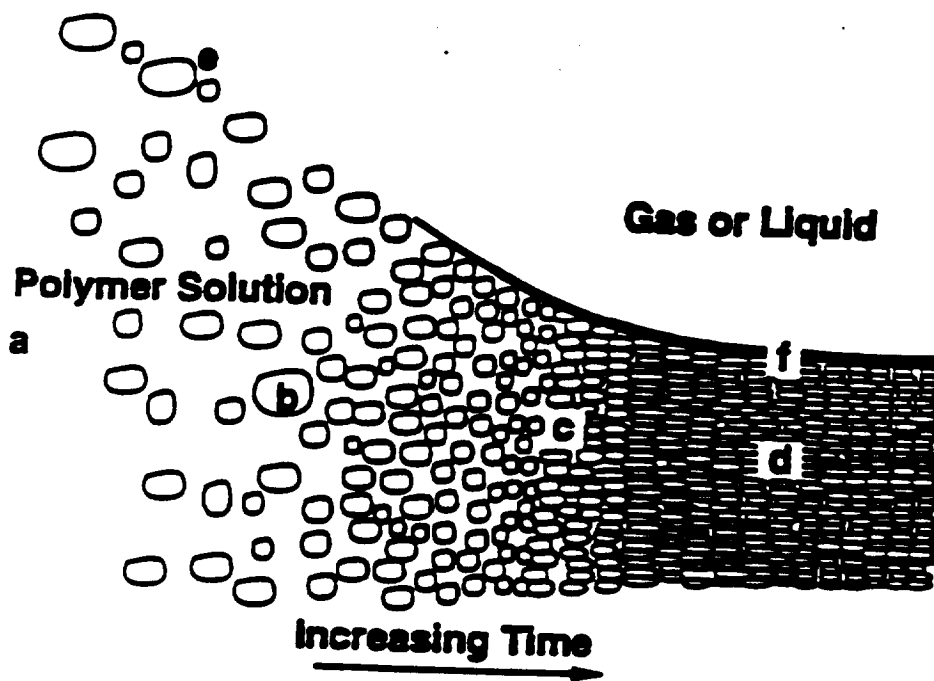


Figure 1: Pictorial representation of the phase-inversion process.

a: Polymer solution continuum, b: water-rich phase drops, c: polymer becomes majority phase, d: coalesced, evaporated water-rich (pore forming) drops, f: thin, dense polymer film or "skin"

Dry casting: : Dry casting is the process on which this study concentrates because of the relative ease of adapting this process to the problem (macrovoid growth) being researched. The dry-cast or complete evaporation process is the oldest of the phase-inversion processes and may be characterized by two macroscopically observable changes. First, loss of both solvent and nonsolvent from an initial ternary homogeneous polymer solution leads to formation of a turbid two-phase solution. Second, solidification follows in which the polymer from the polymer-rich phase precipitates to form a solid matrix which encapsulates the polymer-lean phase. The final membrane thickness is a fraction of the initial cast film thickness owing to both solvent and nonsolvent loss and excess volume-of-mixing effects. Clearly the dry-cast process is accompanied by coupled heat and mass transport. Figure 2 is a schematic representation of the dry-cast process. In summary, in dry casting the phase inversion is brought about by the evaporation of solvent and nonsolvent from an initially homogeneous polymer solution.

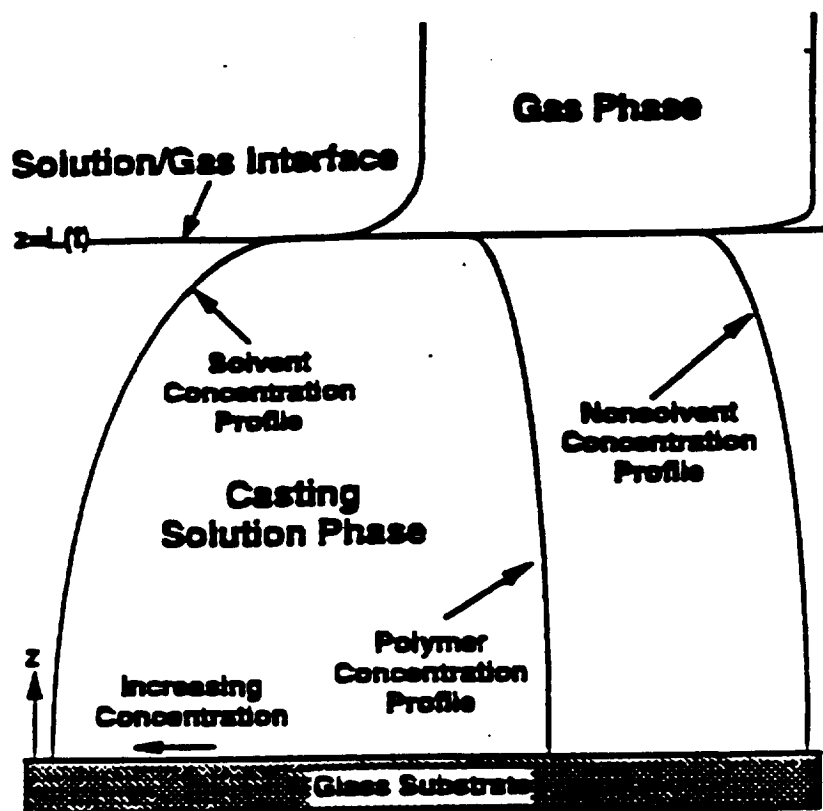


Figure 2: Schematic representation of the evaporative casting of a dry-cast membrane showing horizontal interfaces and concentration profiles of the three components (Reproduced from Shojaie *et al.*, 1993).

Wet casting: The wet-cast process, in contrast to the dry-cast process, is marked by rapid mass transport. The initial cast polymer solution may be subjected to an optional evaporation step. This step then is followed by immersion of the polymer solution into a nonsolvent or precipitation bath in which rapid mass transfer of solvent and nonsolvent between the polymer solution and the bath leads to the formation of the membrane. The wet-cast process may be considered an isothermal process in which mass transfer is the only driving force to bring about phase separation. The current study deals with macrovoid growth in the dry-cast process only.

1.2 Motivation for this study

An inherent difficulty in the manufacture of polymeric membranes is the formation of undesirable structural features which can cause poor performance. The formation of macrovoid (MV) defects during the phase-inversion process is a problem, as macrovoids affect the permeability and mechanical properties of the resulting polymeric membranes. Figure 3 shows a cross-sectional view of a cellulose

acetate membrane showing a dense top layer or "skin" and a porous sublayer with larger macrovoid pores. The presence of macrovoid pores in large numbers can result in compaction and/or collapse of polymeric membranes and hence in a reduction of flux in high pressure applications such as reverse osmosis. Therefore, it is desirable to control the final membrane morphology by optimizing the casting conditions. It has long been known that macrovoids will occur in polymeric membranes formed via the wet-cast process if the nonsolvent/solvent exchange is very rapid. Unfortunately, this rapid exchange is also the condition needed to create a thin dense permselective skin at the surface of the membrane. Hence, in order to avoid macrovoid formation, a compromise is made whereby thicker skin layers are tolerated than would be desired to obtain the maximum permeation rates through the membrane (Sourirajan and Matsuura, 1984). If more could be learned about the nature and causes of macrovoid formation, it might be possible to obtain very thin permselective skin layers while avoiding macrovoid formation. Macrovoid pores are observed in both the dry-cast and wet-cast processes. The development of membrane formation processes that eliminate MVs is important to the rapidly-growing membrane industry.

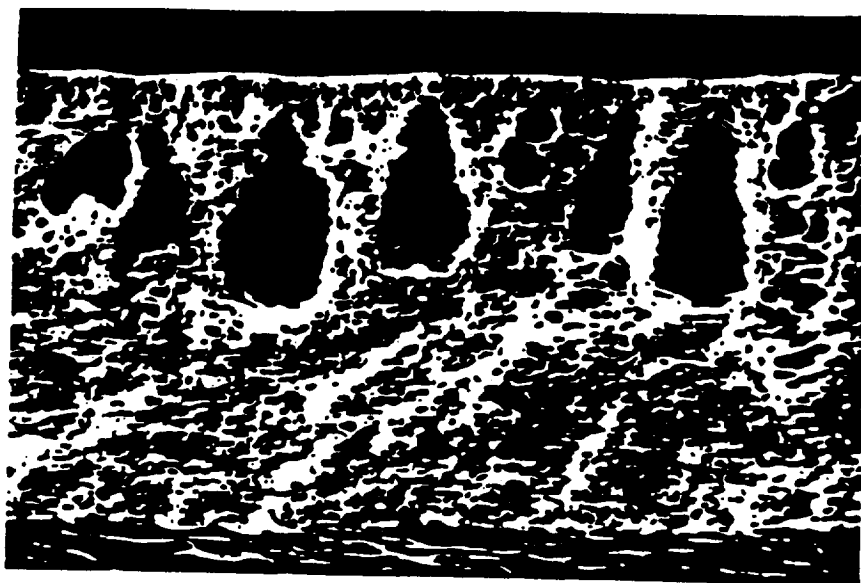


Figure 3 : Scanning Electron Micrograph (SEM) of a cellulose acetate membrane showing macrovoids

1.3 Mechanisms of macrovoid growth

1.3a Liquid-Liquid Demixing Hypothesis for Macrovoid Formation

There are two contrasting hypotheses concerning the mechanism of MV growth, and experimental tests to date cannot distinguish between them. Reuvers (1987) has proposed a liquid-liquid demixing and diffusional transport mechanism based on his studies of macrovoid formation in the wet-cast process. Liquid-liquid demixing is characterized by the onset of phase separation which either occurs very shortly

after the polymer solution is contacted with the nonsolvent bath (instantaneous demixing), or is delayed for a certain period of time (delayed demixing). Reuvers maintains that macrovoids are observed only for instantaneous demixing. He proposes that macrovoids begin to form from nuclei resulting from liquid-liquid demixing just beneath the surface. In this hypothesis the macrovoids grow (ripen) downward into the casting solution by pure molecular diffusion from the surrounding casting solution rather than being "pulled" downward by any type of force such as might arise from interfacial tension gradients. Since only diffusion and no force balance is implicit, the mechanism for macrovoid growth embodied in this hypothesis would not be influenced by body forces such as gravity. The initial demixing process involved in this hypothesis (nucleation which is common to both hypotheses) could possibly be influenced by body forces, although one might anticipate the effect of body forces to be negligible owing to the insignificant mass of the nuclei.

1.3b Solutocapillary Convection Hypothesis for Macrovoid Formation

Shojaie (1992) has proposed a solutocapillary convection mechanism for the growth of macrovoids based on his studies of their formation in the dry-cast process using cellulose acetate (CA)/acetone/water casting solutions. He contends that the hypothesis of Reuvers is questionable owing to the inability of purely diffusive transport to facilitate macrovoid growth on time scales which he observed to be as short as 2-5 seconds. In Shojaie's hypothesis the growth of nuclei into macrovoids is facilitated by solutocapillary convection induced by a higher water concentration at the liquid-gas interface where the acetone is evaporating. The latter creates a surface-tension gradient which "pulls" the growing macrovoid downward into a richer acetone environment; macrovoid growth then is facilitated by convective-diffusion owing to the bulk flow induced by the interfacial (solutal Marangoni) convection. Figure 4 is a schematic diagram depicting these mechanisms. Figure 4a shows the top layer of a cast polymer solution which is undergoing a phase separation via the nucleation and growth mechanism. Each nucleating site has the potential of growing larger and finally becoming a macrovoid. Any proposed growth mechanism must be one that is able to transfer mass to the nucleation sites rapidly, since the macrovoid formation process only lasts from 2 to 5 seconds; a purely diffusive process cannot supply mass sufficiently rapidly to permit this rapid macrovoid growth. Figure 4b depicts the growth mechanism. A nascent nucleus in the region of the polymer solution which is undergoing phase separation is exposed to an environment that is richer in water at the top of the nucleus (the side that is closer to the solution-gas interface) than the bottom. Water has a much higher surface tension than either the acetone or cellulose acetate. Thus, one expects to observe a decreasing surface tension from the top to the bottom of the nucleus. The high and low surface tensions are designated by the symbols γ_H and γ_L in figure 4b, respectively. Under these conditions it is possible to establish a surface-tension-driven or marangoni flow. The Marangoni flow then can convect mass from the

low surface tension to high surface tension region. The advection of mass by the Marangoni flow propels the droplet toward the solid/solution interface.

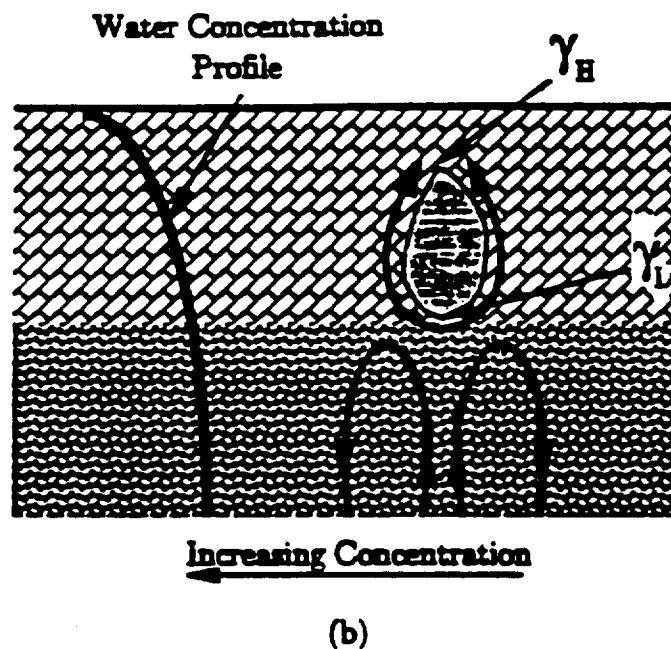
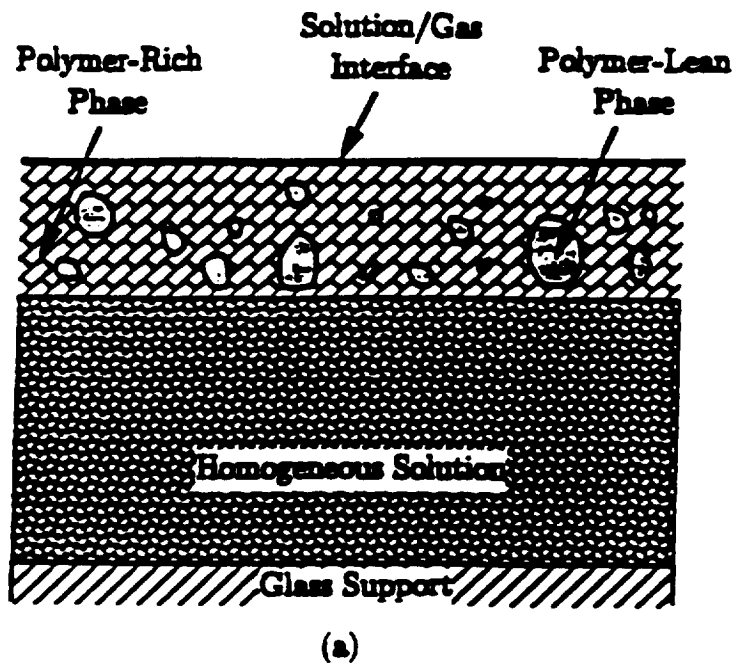


Figure 4: Schematic showing (a) initiation and (b) growth mechanisms for formation of macrovoids in the dry - cast process.

Complementary advection in the adjacent homogenous polymer solution then can supply the growing nucleus with mass. The growth process continues until either the solid-solution interface is reached or the growing nucleus is frozen in place by the solidifying polymer matrix. Macrovoid growth is opposed by both viscous drag and by buoyancy forces since the macrovoid is less dense than the surrounding casting solution. Shojaie used his fully predictive model for dry-casting (Shojaie et al., 1992, 1993) to demonstrate that macrovoids form when reasonably large water concentration gradients exist, but their formation is suppressed when these gradients are not significant. Furthermore, he showed that large gradients in the water concentration occur when the initial casting solution composition is reasonably close to the binodal in the ternary phase diagram for this system. For example, Figure 5 shows the ternary phase diagram for the CA/acetone/water system; the heavy solid line within this diagram defines the binodal envelope wherein phase transition by nucleation and growth becomes possible; the dotted line defines the spinodal envelope wherein spontaneous demixing occurs. The points denoted by 1 through 6 correspond to initial casting-solution compositions studied by Shojaie; macrovoids were observed only for the composition corresponding to point 5 for which Shojaie's model predicted the largest water concentration gradients which would correspond to the largest surface-tension gradients at the macrovoid surface.

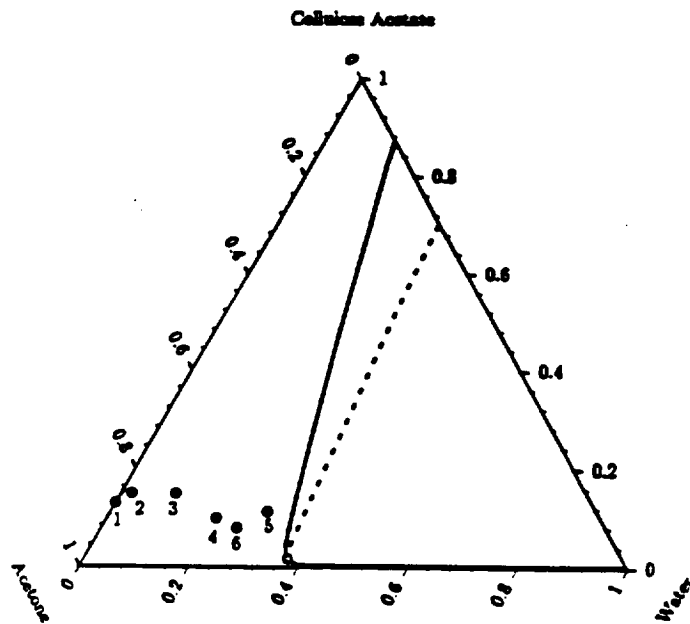


Figure 5: Ternary phase diagram for CA/acetone/water system.

1.4 Low-gravity processing:

The two hypotheses offered to explain the growth of macrovoids are distinguished by the fact that the hypothesis of Reuvers does not involve the significant influence of body forces; in contrast, the hypothesis of Shojaie involves a mechanism that is strongly influenced by body forces. Hence, casting polymeric membranes in a reduced inertial environment (low g) should permit

discriminating between these two mechanisms. In particular, by reducing the gravitational acceleration, the resisting buoyancy forces will be reduced; this should result in more rapid macrovoid growth which should be verifiable via greater macrovoid penetration into the casting solution and possibly via an altered macrovoid shape. Moreover, by reducing the buoyancy forces, it should be possible to cause macrovoid formation for casting-solution conditions which did not result in macrovoid formation in the earth's gravitational field; observing the latter would provide a particularly discriminating test of these two hypotheses in order to determine which (if either) is correct. Experiments in a reduced gravity environment were proposed in which buoyancy forces would be modified by varying the inertial acceleration vector. After reviewing the various methods in which one could obtain reduced gravity and conduct meaningful experiments, experiments involving the dry-casting of CA membranes in low gravity on the NASA KC-135 aircraft were performed. Table 1 shows the various experiment accommodations provided by NASA.

Table 1

Approximate Experiment Accommodations Provided by NASA

	DROP FACILITY:	AIRCRAFT:	ROCKET:	SHUTTLE:	SPACE STATION:
Low Gravity Range --	.10 ⁻⁶ g	10 ⁻⁴ g	10 ⁻⁵ g	10 ⁻⁶ g	10 ⁻⁶ g (microgravity)
Low Gravity Period --	2 - 5 sec.	20 - 25 sec.	5 - 14 min.	7 - 16 days	45 days or more
Exp. Hardware Size --	Up to 1m ³	Several m ³	Up to 1m ³	Drawers 1m ³ and Lab Racks (1/2m x 2m)	Multiple Lab Racks 1m ³ per rack
Exp. Hardware Mass --	Several 100 kg	Several 1000 kg	Up to 500 kg	Up to several 100 kg	700 kg per rack
Exp. Hardware Type --	PI-specific	PI-specific	PI-specific	Multiple User Experiment Facilities with PI-specific modules	
Microgravity Program --	← Ground-Based Research Program →				← Space Flight Experimentation Program →

A glance at the table shows that in the time-frame of a M.S curriculum the best experiments could be performed on board the KC-135 low-gravity aircraft. The KC-135 is a NASA-owned turbojet which flies through a series of parabolic maneuvers resulting in short periods (approx. 20 seconds) of nearly zero g acceleration. Figure 6 shows the side view of the KC-135 and the trajectory of its flight. The duration of the parabola is around 25 -30 seconds, and the acceleration levels are in the order of 0.001g. The resulting reduction in buoyancy forces is expected to exaggerate the MV formation process, because buoyancy should oppose solutocapillary motion in the presence of 1 g, but not in low g.

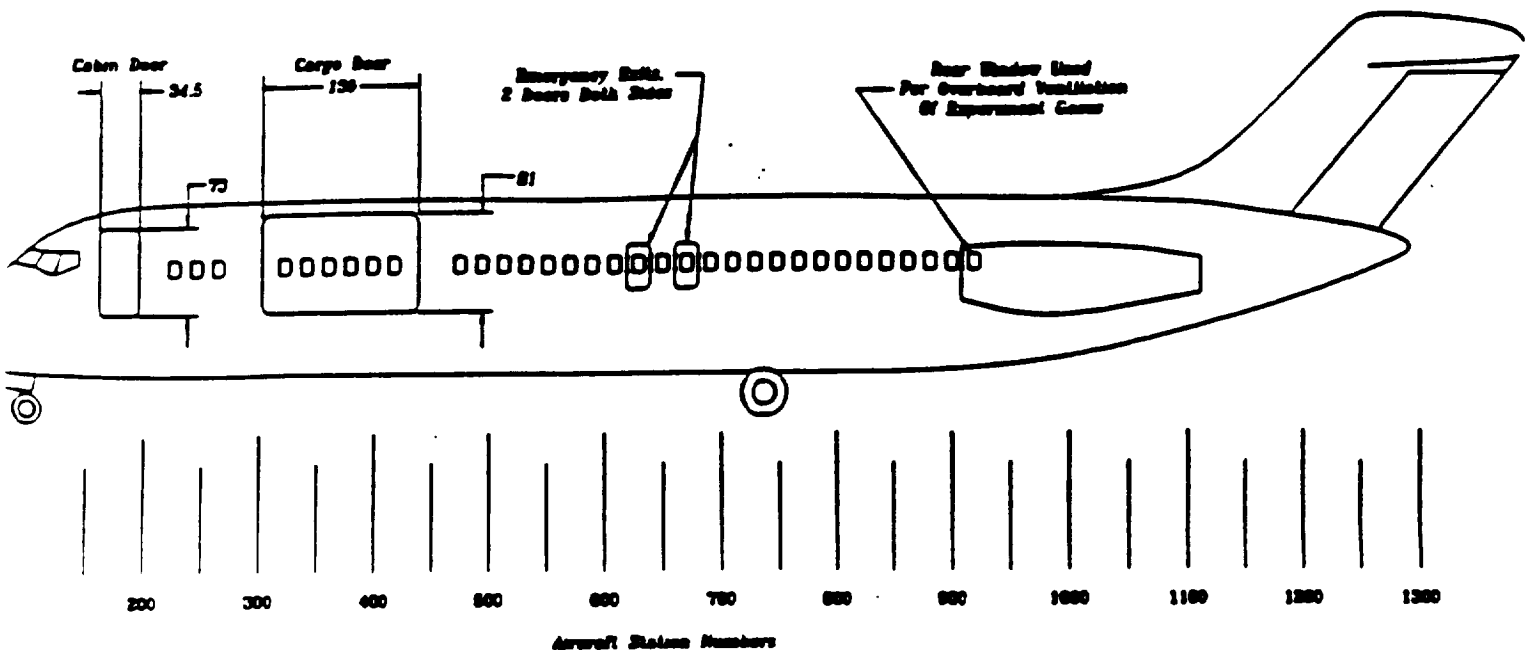


Figure 6 a : Side view of the KC-135 (Dimensions are in inches)

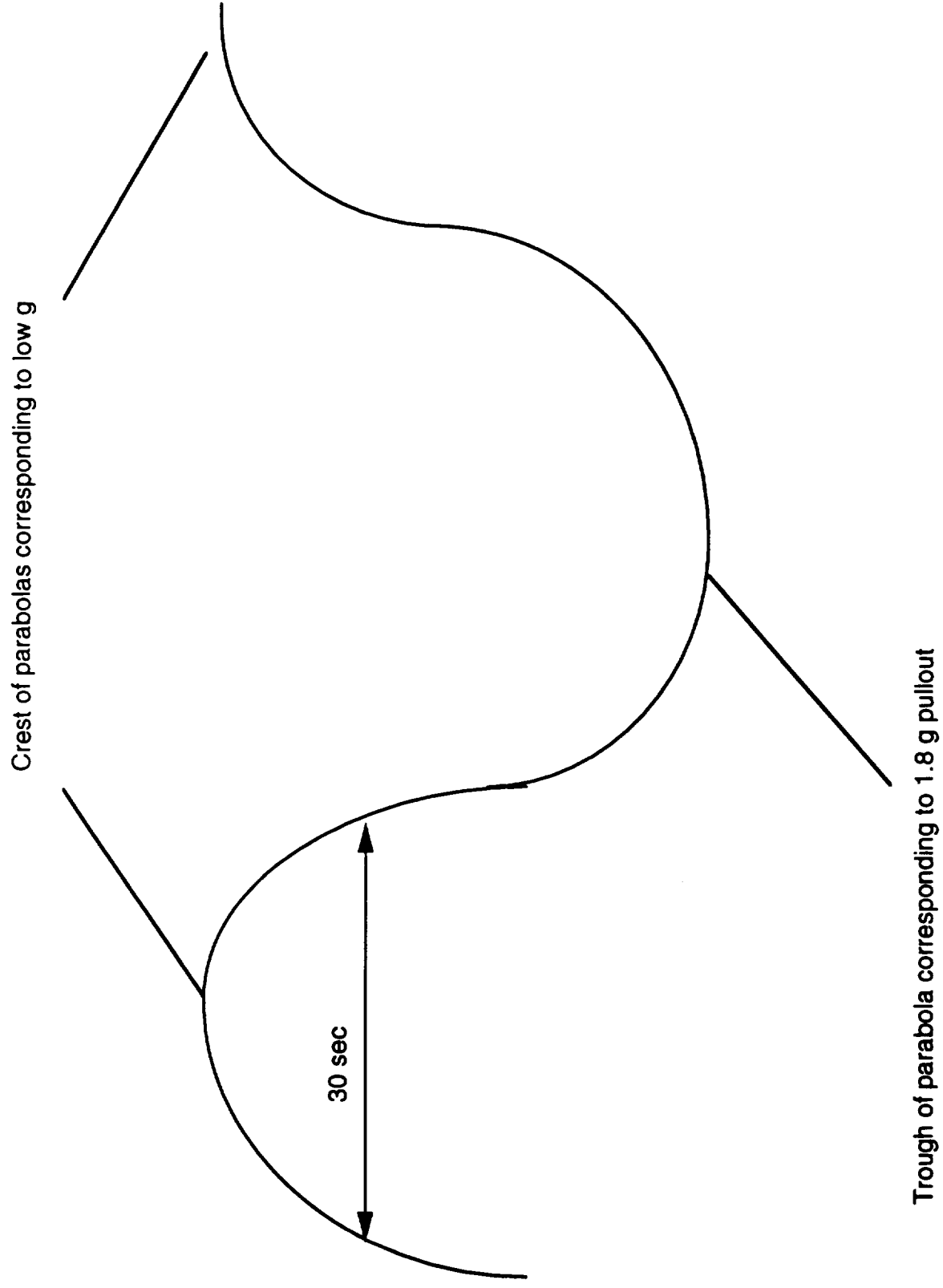


Figure 6b: Parabolic flight trajectory of the KC-135

2 Materials and Experimental Design

2.1. Design considerations

A dry casting system was used because it is simpler than wet casting to operate in low g. Casting solutions were prepared from mixtures of CA, acetone, and water based on the model predictions of Shojaie *et al.* (1993) using the ternary phase diagram such as shown in Figure 5. Compositions were selected to insure that the phase-transition process and MV growth occurred well within the limited low g time available on a KC-135 flight (20 secs). Typical casting-solution compositions were 10-15 wt.% CA, 55-65 wt.% acetone, and 20-30 wt.% water. The KC-135 flies in a series of parabolic arcs with each parabola being initiated with a 1.8-g pull-up and terminated with up to a 1.8-g pull-out. Since this permitted both low g as well as enhanced g environments, some membranes were also cast during the high g part of the cycle.

2.2 Membrane Casting Solution

CA (Eastman 398-10 with a MW of 40,000 and DS of 2.45) was dried at 110 °C under vacuum for several days. Reagent-grade acetone (Baker, Inc.) was used as received. De-ionized distilled water was used in preparing the polymer solutions which were mixed (minimum of 8 hours) with a magnetic stirrer. In order to avoid premature phase separation during preflight storage the solutions were ultracentrifuged at 10,000 rpm for one hour in a sorvall RC-5C plus centrifuge to remove any undissolved polymer and the heavy end of the polymer molecular weight distribution. The supernatant was immersed in a bath of methyl alcohol to precipitate the remaining dissolved polymer. The polymer was collected by vacuum filtration, and the retentate was dried in a vacuum oven at 60°C for two hours. The desired casting solution compositions in the range 10-15 wt.% CA, 55-65 wt.% acetone, and 20-30 wt.% water then were made from this regenerated dried polymer; the resulting casting solutions were found to be stable against phase separation for at least one week.

2.3 Membrane Casting Apparatus

The experimental principle is shown in figure 7. The membranes were cast using a Membrane-Casting Apparatus (MCA) which works on the sliding block principle. A chimney full of polymer solution is held over a casting well 100-250 μm deep. The casting well is set in the sliding block which is driven using spring-loaded ball plungers. The schematic of the MCA is shown in figure 8. When the pin that retains the compressed springs is removed, the ball plungers impulsively move forward to align the casting solution in casting cavity B (figure 7) with an adjacent chimney C filled with activated carbon. At this point solvent evaporation begins and will continue until evaporation is complete (dry casting). When a sufficient amount of acetone has evaporated, the membrane forms in the well B below. Each

MCA has six casting wells in the sliding block; four such MCAs were used during the low g flights. Films were cast in wells 100, 150 and 200 μm deep.

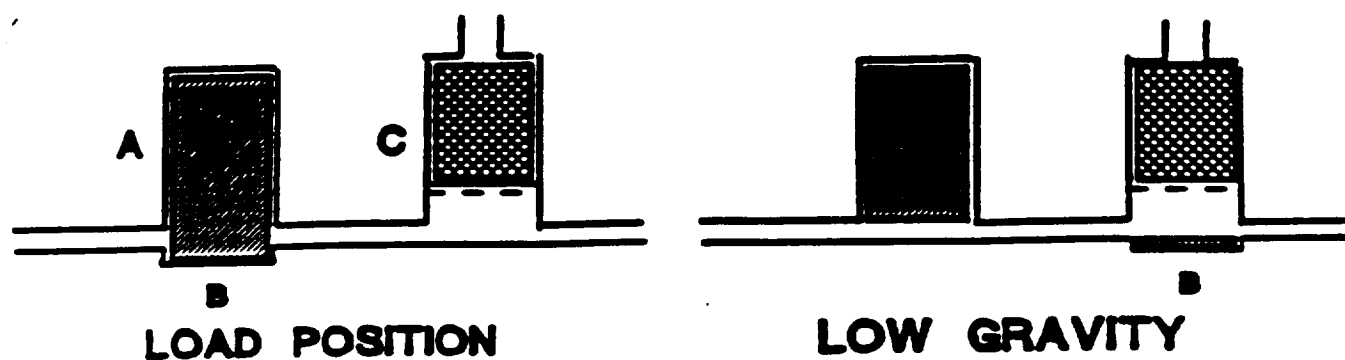


Figure 7: Membrane-casting apparatus (MCA). Left: opposing cylinders positioned for loading. Right: Positioned for membrane casting. A: Chimney filled with casting solution. B: Casting cavity. C: Chimney of activated carbon absorbant

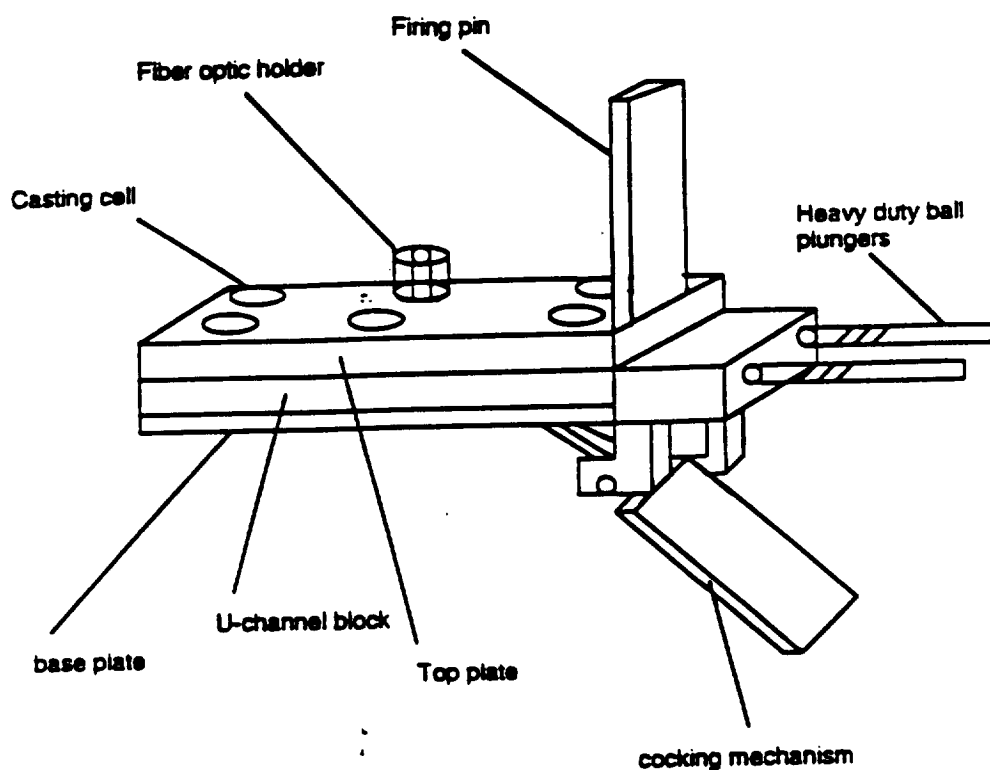


Figure 8 : Schematic of the Membrane Casting Apparatus (MCA)

Polymeric membrane formation via the phase-inversion process is marked by the transition from an initially transparent polymer solution to an opaque white polymeric membrane. Therefore, a light-reflectometry analysis can take advantage of the changing light-reflection properties of the cast polymer solution in order to provide information regarding phase inversion. Again, the concern regarding the noninvasive nature of this measurement is satisfied, since the detection of changes in the light intensity does not require physical contact with the polymer solution. This technique is used to detect the onset and duration of phase transition. Figure 9 is a schematic of the light reflectometry technique. The light-reflection apparatus utilized in this study consisted of a DC-regulated broad-band quartz-halogen-light source (Oriel Model 77501), a bifurcated fiber-optic cable (Oriel Model 77533), photodiode(PIN # 10DP United Detector Technology), and a personal computer equipped with an A/D convertor and signal amplifier. The light source emits radiation in a broad spectral band ($0.3\text{--}1.8\ \mu\text{m}$) which encompasses visible as well as near-infrared radiation. The light is directed toward the surface of the cast polymer solution using one of the bifurcated fiber-optic legs. The light then is collimated and directed at an angle normal to the surface of the cast polymer solution. Any changes in the intensity of the reflected light are detected by a photo diode which is mounted at the end of the return leg of the bifurcated fiber-optic cable. The photo diode converts the light intensity into an electrical current which in turn is converted into a voltage signal which can be stored on the personal computer . An infrared filter(Model 51962) with a 70% transmission from a wavelength of 0.3 to 0.8 micron was used in all the subsequent experiments to prevent any radiative heating.

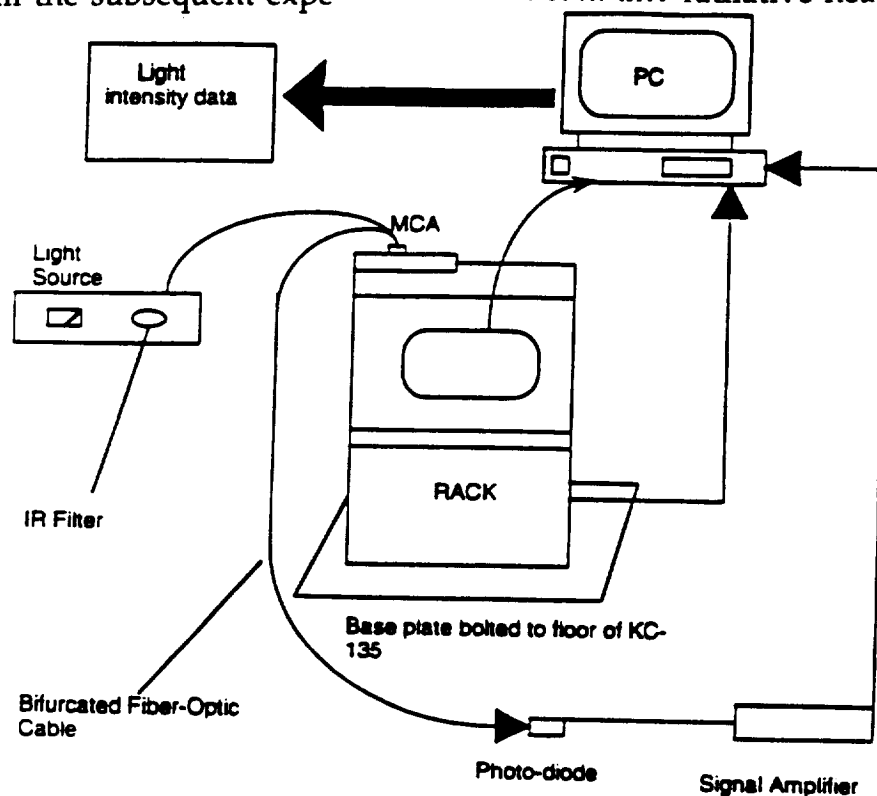


Figure 9 : Schematic of the light-reflectometry experiments as arranged for low-gravity experiments

The Personal Computer along with the fiber-optic system was mounted on a standard rack of dimensions 21 in. x 15 in. x 28 in. This rack was in turn mounted on a base plate anchored to the floor of the KC-135 after clearing NASA safety regulations. The MCA's were mounted on top of the rack as was the fibre-optic illuminator-detector..

2.4 Morphological Analysis

All samples were allowed to air-dry for 3 additional hours at the end of optical data acquisition in the MCA which typically took about 2 to 5 minutes. At the end of air drying, the dense polymer films or membranes were separated from the MCA Delrin support. Samples were dried further under vacuum for one day at ambient temperature. Cross-sections of the samples were prepared by freeze-fracturing them under liquid nitrogen. Finally, the samples were coated with gold using a Denton (DV-502A) evaporative coating system. The membrane structure was examined to discern any differences in the prominence and geometry of the MVs formed under low g and ground-based conditions.

2.5 Low gravity procedure

The conduct of experiments on board the KC-135 aircraft entailed meeting numerous preliminary requirements. Mr. Konagurthu, underwent an Airforce class 3 flight physical examination and met the requirements of the USAF physiological training program. This was accomplished at the Peterson AFB, Colorado Springs. The entire test equipment underwent a safety and TRR (Test Readiness Review). After the above requirements were met, the experiments in low g were performed on board the KC-135 aircraft of NASA at the Johnson Space Center and Ellington Field in Houston, TX. Flights were performed over a week in March 1995. The KC-135 typically flew around 40 parabolas each day. The low-g time available was typically approximately 20-30 seconds per excursion, which accommodated the time predicted for phase inversion. A special request was made and permission was obtained to fly extended parabolas in order to get increased low-g time. Approximately 100 membranes of thicknesses 100, 150 and 200 μm were cast during flights corresponding to the same thicknesses employed for morphological studies in the control experiments. The compositions studied were in the range 10–15 wt% CA, 55–65 wt% acetone, and 20–30 wt% water - the same as those employed for the ground based control experiments. The MCAs, the fiber-optic system, the PC for storing the light-intensity data, an ambient temperature probe, and a g sensor which showed the acceleration levels were mounted in the electronics rack bolted to the floor of the aircraft. The membranes were cast as soon as the g sensor indicated the appropriate level of acceleration. Figure 10 shows a typical plot of the acceleration levels recorded during the 3rd parabola of the 1st flight. During low g the

MCAs were allowed to free float in the cabin of the aircraft in order to eliminate the possibility of vibrational effects which might have arisen had they remained fixed to the electronics rack.

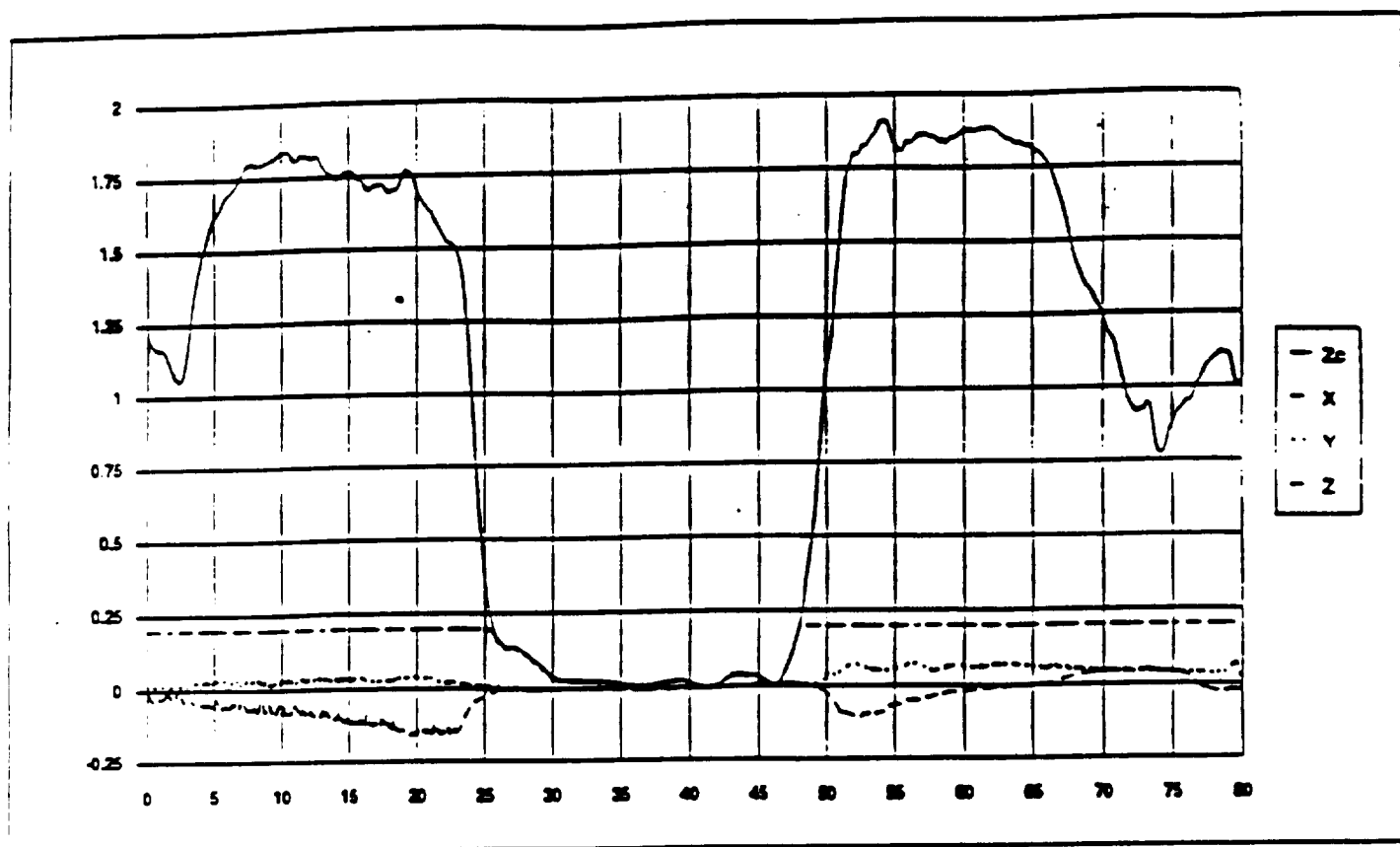


Figure 10: Plots of acceleration levels recorded during the 3rd parabola of the 1st flight. Vertical axis in g; horizontal in seconds; data filtered at 10 Hz.

3 Results

3.1 Morphological studies

All the electron micrographs of the membranes shown in this section are cross-sectional views with the initial casting solution-gas interface facing upward. Figure 11 shows a concentration map of initial polymer composition solutions that have been observed to form macrovoids.

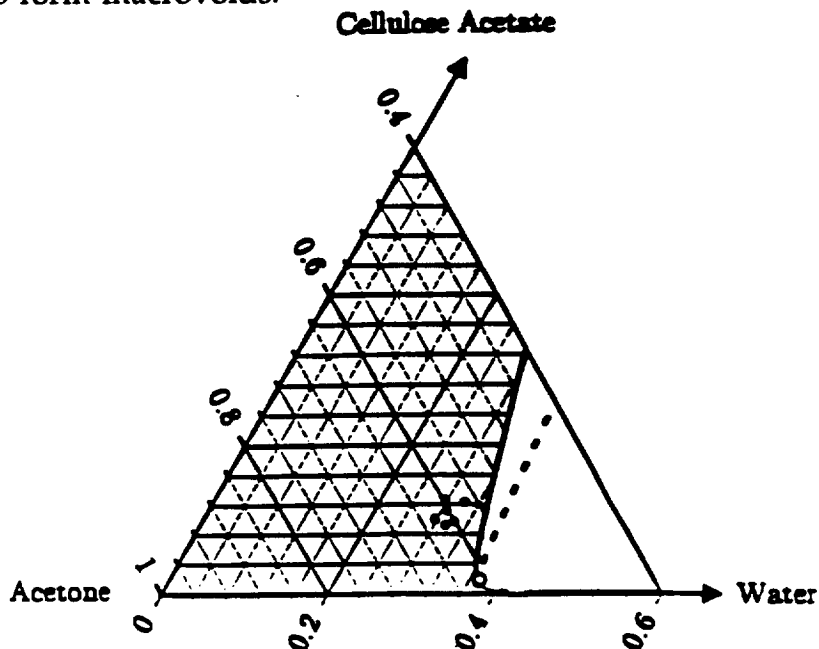


Figure 11: A concentration map showing a region (•) of the ternary phase diagram where MVs have been observed during the dry-casting of polymeric membranes

Figure 12a shows the cross-section of a typical membrane of thickness 100 μm cast on the ground. SEM analysis shows that MVs are observed, but they are sparse and scattered as the figure indicates. This was the general trend observed on all the ground-based experiments. The MVs formed were in general widely spaced but were more than average in number. Figure 12b shows a typical cross-section of a membrane having the same thickness and composition, but cast in low-g. MVs are present throughout these membranes. The MVs are densely packed as compared to those in the ground based one. This was a general trend observed in the membranes cast in low g. MVs were more numerous, more regular and occasionally larger than those cast in the laboratory. Figure 12c shows the cross-section of a membrane cast in high-g having the same thickness and composition as employed in the 1-g and zero g experiments. As can be seen, no MVs are observed. Most of the membranes cast in high-g did not appear to contain macrovoids over the same distance as were

observed in the low g and ground based membranes. In some of the low-g membranes the MVs penetrated through to the bottom of the membrane.

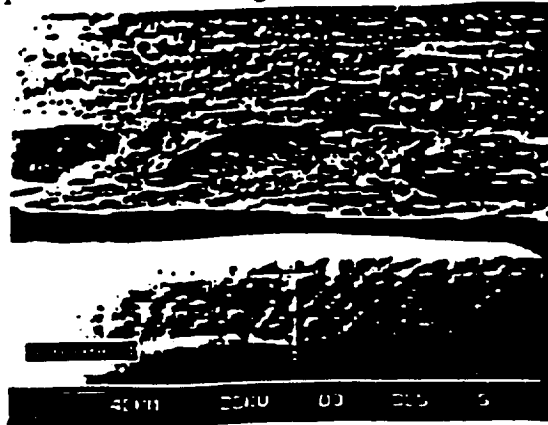


Figure 12a: Representative cross-section of a membrane cast on ground showing sparse MVs

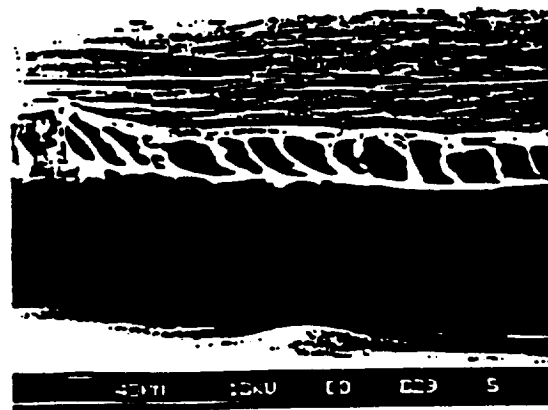


Figure 12b: Representative cross-section of a membrane cast on ground showing large, densely packed MVs

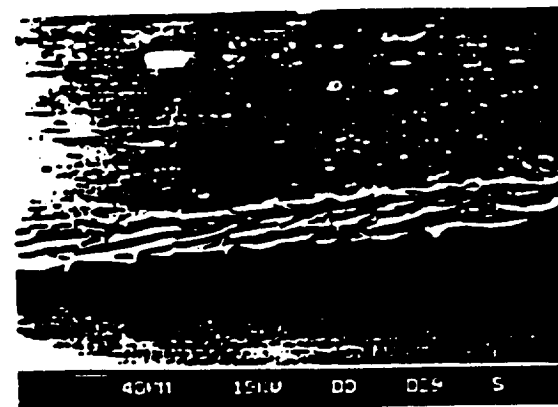


Figure 12c: Representative cross-section of a membrane cast in high-g; no MVs are present

3.2 Reflectometry Data

In order to observe the progress of the phase inversion during the low g experiments, the optical reflectance of the forming membranes was measured as a function of time during each parabola. Figure 14 is a record of the reflected light intensity as a function of time after the onset of low g during a typical parabolic excursion. The initial casting solution composition was 10 wt% CA, 30 wt% water, 60 wt% acetone.

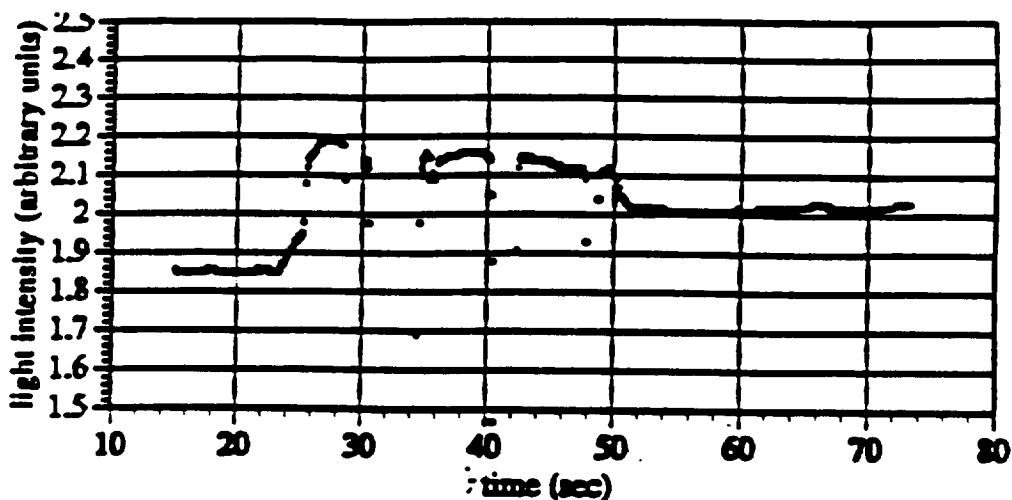


Figure 13: Typical output of light intensity versus time in low gravity showing the onset of phase inversion (signal rise) and subsequent completion of phase transition (signal fall). The low-g onset is at 23 sec. on the plot.

The thickness of the membrane was 100 microns. Initially, the light intensity is constant prior to activation of the slide mechanism which initiated the membrane-casting process. As soon as casting was initiated, there was a sharp rise in the light intensity, corresponding to the formation of a highly reflecting gel layer (specular reflection). The subsequent decrease in intensity is due to the formation of nuclei of the dispersed polymer-lean phase corresponding to the upper surface of the casting solution entering the phase envelope. The later monotonic decrease is due to the lower regions of the casting solution entering into the phase envelope, thereby creating more nuclei and MVs which scatter light. Eventually the casting solution at the very bottom of the well enters the phase envelope. Once this occurs the light intensity becomes constant again. We believe these are the first experiments in which real-time data have been obtained for membrane casting in low g. Figure 14 shows a typical output of light intensity versus time after casting at 1 g for a 100 micron- thick membrane having the same initial composition as that of the low g membrane casting experiments discussed above. The pattern of initial increase in light intensity because of the formation a highly reflecting gel layer and the subsequent decrease due to the nuclei in the lower regions scattering light is mirrored in the low g experiments.

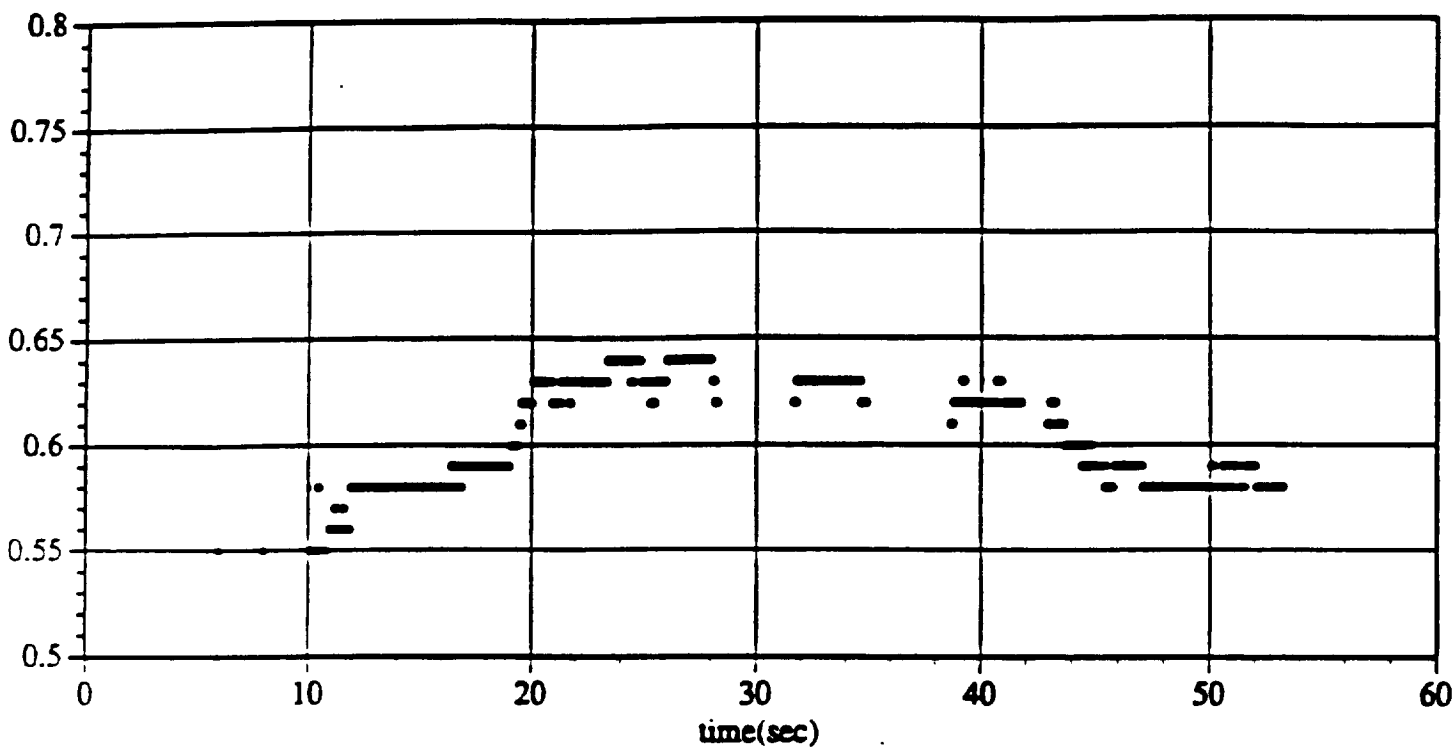


Figure 14: Typical output of light intensity versus time in 1 g (ground) showing the onset of phase inversion at 18 sec. and the subsequent completion of phase transition at 44 sec.

The time required to initiate phase transition and the duration of the phase transition process is the same for identical initial casting solution compositions and membrane thickness as evidenced by figures 13 and 14. This was to be expected because the evaporation and transport of the solvent (acetone), which in turn determines the inception and duration of phase transition process is diffusion driven. However, the exact shape is not reproduced at 1 g and low g because of the presence of increased macrovoids in the low g as compared to the ground based control experiments. Intensity data could not be obtained in high g because the computer drive could not withstand the force, and data could not be acquired.

A mathematical model (described below) is currently being constructed in order to predict the time required for the casting solution to enter the phase envelope; note that the liquid/gas interface will enter the phase envelope first; the casting solution at increasing depth beneath the interface will enter the phase envelope at progressively increasing times. Hence, the model can also predict the duration of the phase transition which corresponds to the time required for the casting solution at the lower solid support to enter the phase envelope. These two quantitative predictions then can be compared to the results obtained from the light-reflection measurements.

4. Discussion

4.1 Comparison of hypotheses

The above results clearly favor the hypothesis of Shojaie et al. (1992, 1993) as compared to the contrasting hypothesis of Reuvers (1987). We found that membrane formation in low g in the absence of buoyancy forces causes an observable change in the geometry and growth of macrovoids. The Macrovoids formed in low g occurred much more frequently, were occasionally larger and penetrated further down into the casting solution. Hence a reduction in body forces caused macrovoid growth more readily. In fact a monotonic g - dependence of MV formation was observed. The optical monitoring data were also found to be consistent with the hypothesis of Shojaie et al. (1992, 1993). These studies appear to be the first quantitative studies of membrane casting in micro-gravity which incorporate real-time data acquisition.

4.2 Model Development

4.2 a Adaptation to MCA geometry and low gravity

The model development task is subdivided into two related subtasks. First, in order to interpret both the ground-based and low-g experiments, it was necessary to modify the evaporative casting model developed by Shojaie, Krantz, and Greenberg (SKG model), (1992, 1993) to incorporate the gas-phase mass and heat-transfer characteristics appropriate to the casting apparatus used in these experiments. Shojaie et al. modeled the gas-phase mass and heat transfer appropriate to the casting apparatus used in their experiments; this was free-convection mass transfer of a less dense volatile component into a gas phase above a square interface. They

chose this mass-transfer geometry because it is described by the heat-transfer correlation for a cooled square plate facing upwards. Since we want the gas-phase mass and heat transfer to be the same for both our ground-based and low-g experiments, we could not employ the mass-transfer geometry used by Shojaie et al., since any free convection effects should be quite small for the low-g experiments. Hence, we modified Shojaie et al.'s model to incorporate the gas-phase mass and heat transfer appropriate to the design of the MCA. This corresponds to purely diffusive mass transfer from the liquid/gas interface across the thin gas layer to the activated carbon adsorbent. Incorporating this gas-phase mass and heat transfer into the model of Shojaie et al. has been done and the appropriate modifications to the model to account for the changed boundary conditions has been performed. We also modeled the heat transfer in the gas phase as pure conduction across the gas layer in low g. As we anticipated, that heat-transfer effects were quite small for these experiments since the casting-solution compositions are such that the phase envelope is entered quite rapidly, thereby precluding any significant cooling effects owing to evaporation. The model predicts that steep water concentrations are indeed a pre-requisite for MV formation. The model predictions were corroborated using the technique of Laser interferometry and the fit between the model and experiments is quite good (Konagurthu *et al.* (1996)). We have submitted a manuscript highlighting the robustness and the applicability of the SKG model for dry-cast CA-acetone-water membranes to the Journal of Membrane Science.

4.2 b Quantitative Description Of Macrovoid Growth

Since the low-g experiments and the SKG model indicate that the hypothesis advanced by Shojaie for macrovoid formation is correct, it would be of considerable value to develop a quantitative model for macrovoid growth. This will consist of a force balance which incorporates the solutocapillary, viscous drag, and buoyancy forces; acceleration effects can be shown to be negligible for the small masses involved in MV growth. Although the MVs grow on a very short time scale, they are very small (typically < 200 microns); hence, the viscous drag can be determined using a Stokes flow approximation appropriate to very low Reynolds numbers. The solutocapillary force will be determined using standard methods as described by Legros et al. (1990) and others. This will require estimating the surface-tension gradient along the surface of the macrovoid. Here we propose to use the model of Shojaie et al. (1992, 1993) (appropriately modified to account for the gas-phase mass transfer of these experiments) in order to determine the far-field concentration profiles. We then propose to use a lumped-parameter description of the mass transfer to the growing macrovoid which allows for both diffusive and advective transport. Determining the buoyancy force is reasonably straightforward; however, its determination is also coupled with the mass transfer since macrovoid growth and shape must be accounted for. Assuming an axisymmetric geometry for the macrovoids (i.e., see Figure 3) will simplify this model development considerably. The biggest challenge here is in developing an adequate description of the mass transfer to the growing macrovoid since this influences the surface-tension gradient as well as the size of the macrovoid.

4.3 Implications for Commercial Membrane Industry

The final goal of this study is to show how the experimental technique and the models developed can be used to improve the commercial fabrication of membranes. The experimental studies clearly show that macrovoid formation is enhanced by a reduction in buoyancy forces. These studies suggest that it could be advantageous to employ centrifugal acceleration while casting membranes in order to create a thinner dense permselective skin while avoiding macrovoid formation. The technology exists to do this since centrifugal acceleration is employed in the flood-Gravure process for manufacturing photoconductive films. Surprisingly, to the best of our knowledge, no one has considered using centrifugal force to mitigate macrovoid formation in polymeric membrane formation! Since these low-g experiments reveal that reducing downward inertial acceleration promotes MV formation, the experiments will provide strong support for designing a membrane-casting apparatus which employs enhanced acceleration to suppress MV formation under conditions for which heretofore it could not be avoided. This enhanced acceleration could be achieved by casting the membrane on the outer surface of the support film which passes over a rapidly rotating roller such as is used in the flood-Gravure process. Such a process could result in much thinner skin layers which would yield the same selective permeation properties while permitting higher permeation fluxes.

5. Conclusions

Based on the micrographs of the cross-sections of representative membranes cast in low g, 1 g and high g, the hypothesis that diffusion is solely responsible for MV growth appears to be tenuous. This study suggests that gravitational body forces do play a significant role in the growth of MVs. Indeed MVs were more prominent in low g than in the ground-based experiments for the same casting conditions and were eliminated by casting under higher g levels. Modeling the process is currently underway. The modeling studies show that higher water concentration gradients (non-solvent) are set-up during MV formation. Laser interferometry results were used to corroborate the model which was found to be robust for the physical system considered in this study. Finally, the reduction of MV growth by reducing the downward acceleration suggests possible engineering solutions to the problem of obtaining thinner skin layers without MVs.

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